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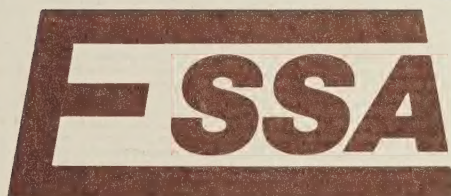
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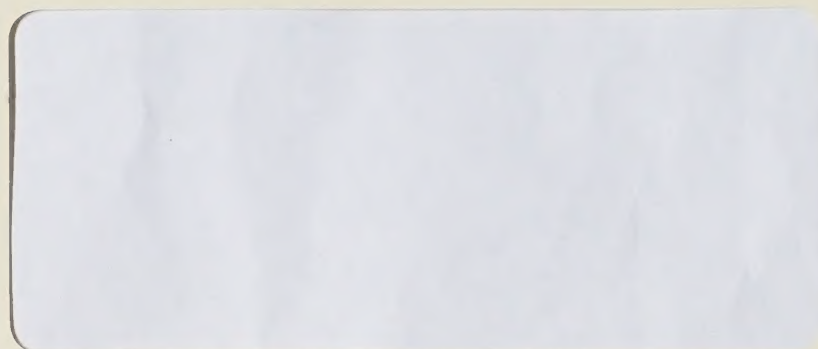
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HYDROELECTRIC RESERVOIRS:
DRAFT REPORT ON A WORKSHOP
HELD APRIL 9 - 11, 1984

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to
Canadian Electrical Association

MERCURY RELEASE IN
HYDROELECTRIC RESERVOIRS:

DRAFT REPORT ON A WORKSHOP
HELD APRIL 9 - 11, 1984

by

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May, 1984



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This draft report is a synthesis of the collective understanding of over twenty five people, each of whom made valuable contributions to the workshop. We acknowledge with thanks their cooperation and hard work.

Authorship of this report is shared by four people, whose contributions are listed below:

Sections 1 and 2: Gina Cunningham

Sections 3, 4 and 5: Gina Cunningham, Lorne Greig, Michael Jones and David Marmorek

Editor: David Marmorek

We are grateful to the Canadian Electrical Association for recognizing the value of the workshop and encouraging representatives of their member utilities to attend.

Finally, we thank Jean Zdenek of ESSA for her excellent work in producing this report, and Sharon Galenzoski for drafting the figures.

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1.0 INTRODUCTION

1.1 Background

Mercury pollution in the aquatic environment has received a great deal of attention over the last decade, particularly since the incidence of mercury poisoning at Minamata Bay, Japan. Within Canada, effluents from a chlor-alkali plant and pulp and paper mill resulted in mercury contamination of the English-Wabigoon River system, threatening commercial fish operations and traditional food supplies of native groups (Jackson et al., 1980).

Recently, another mercury problem has come to light. Newly impounded reservoirs (without any local anthropogenic sources of mercury) contain fish with high levels of this chemical (Cox et al., 1979). This phenomenon has been reported in reservoirs from various parts of Canada, including insular Newfoundland (Bruce and Spencer, 1979), northern Manitoba (Bodaly et al., 1984), and southern Saskatchewan (Waite et al., 1980).

The Canadian Electrical Association decided in 1983 to sponsor a study of mercury release in hydroelectric reservoirs with the following objectives:

- 1) to identify sources and conditions most likely to result in mercury problems;
- 2) to summarize the state-of-the-art knowledge of mercury uptake processes;
- 3) to identify factors leading to greatest mercury bioaccumulation;

- 4) to develop methods for predicting possible mercury problems;
- 5) to provide guidelines for possible mitigative action;
and
- 6) to recommend further research needs.

A prerequisite to achieving these objectives is a synthesis of the current understanding of mercury problems in Canadian hydroelectric reservoirs. To this end, a workshop was held April 9 - 11, 1984 at the Institute for Environmental Studies, University of Toronto. This was attended by representatives of hydroelectric utilities from across Canada and experts familiar with particular aspects of the mercury problem, as well as members of the study team from ESSA Ltd., LGL Ltd., and the University of Toronto (Table 1.1).

1.2 Workshop Proceedings

To establish a common starting point, the participants first developed an explicit definition of the problem to be addressed by the workshop. It was agreed that the "mercury problem" concerned hydroelectric reservoirs where incremental increases in fish mercury concentration (as a result of reservoir construction) create a real or perceived health hazard to humans consuming fish from those reservoirs.

The objectives of the workshop, then, were to:

- 1) develop a conceptual model of the processes by which fish become contaminated with mercury following construction of hydroelectric reservoirs; and
- 2) evaluate the hypotheses within the conceptual model for the purpose of documenting:

Table 1.1: List of participants at the April 9 - 11 workshop.

<u>NAME</u>	<u>AFFILIATION</u>	<u>TELEPHONE</u>
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- a) evidence supporting or refuting the hypotheses;
- b) the value of testing the hypotheses;
- c) alternative methods of testing the hypotheses; and
- d) where feasible (i.e., within the time and financial constraints of the CEA project), develop a preliminary research plan to address identified gaps in current understanding of the mercury problem.

In order to reach a common understanding of mercury release and bioaccumulation processes, and to ensure the problem would be addressed from an applied perspective, most of the first day of the workshop was devoted to a structured procedure known as bounding.

2.0 BOUNDING

Bounding serves to determine a level of concern for a specific problem, and thereby choose the components to be explicitly considered in addressing this level of concern. The level of concern is determined by developing a set of realistic "actions" and "indicators" (defined below) and placing these in an appropriate temporal and spatial framework. The following sections summarize the bounding decisions made by the participants at the mercury workshop.

2.1 Actions

Actions are defined as human interventions in a system. In this case, the primary action of concern was the creation of a reservoir. Both the characteristics of the chosen site and the hydrological features of the reservoir were thought to be the most important influences on the level of mercury ultimately found in fish (Table 2.1).

Decisions concerning reservoir management constituted a second category of actions. The reservoir depth and flushing time, and the frequency, degree, and location of water drawn down could potentially affect the amount of mercury reaching higher trophic levels.

For existing reservoirs with an identified mercury problem, several strategies were suggested as a means of reducing the health hazard to humans consuming fish from the reservoir. Among the mitigative actions suggested were the addition of chemicals and nutrients, resuspension of inorganic sediments, measures controlling the species, age and size of fish present in the reservoir, management of the fish harvest, and processing of fish to remove mercury prior to consumption.

Table 2.1: Actions.

1. Creation of a reservoir

Site characteristics which could influence the amount of mercury methylated and/or bioaccumulated:

- amount of land flooded
- geology of flooded land
- soil type of flooded land
- existing land use
- vegetation type
- climate
- mercury content of soil and vegetation
- erosion potential
- inputs of mercury from atmosphere and anthropogenic sources
- morphometry of reservoir basin
- fish species present
- water quality

2. Management of reservoir

- reservoir depth
- frequency and degree of drawdown
- flow characteristics of reservoir
- flushing time
- location of water draw-top versus bottom water

3. Mitigative actions

- resuspend clay-rich sediments
- add selenium
- cover bottom sediments with inorganic material
- add lime
- add sulphate and sulphite (to get mercurous sulphate)
- add phosphorous and nitrogen to eutrophy system
- stock fish
- regulate harvest of fish
- encourage utilization of non-predatory fish (i.e., containing less mercury)

Table 2.1 (cont'd.):

3. Mitigative actions (cont'd.)

- remove human access to reservoirs
- process fish in such a way as to remove mercury prior to consumption
- control erosion
- remove vegetation in flooded area
- plant tolerant vegetation in drawdown zone (prevent erosion)
- control mercury inputs to system

2.2 Indicators

Indicators are defined as those quantities which are used to evaluate the performance or health of a system in response to a perturbation or set of actions. In view of the uncertainties and regional variation inherent in the mercury problem, it was necessary to consider indicators other than just the mercury concentrations of top carnivore fish. On the other hand, the list of indicators suggested by the participants (Table 2.2) reflected their dominating concern for bioaccumulation of mercury in the aquatic food chain.

Two other indirect indicators were suggested. The first concerned the transformation of inorganic mercury into the more toxic methylated state. The rates of mercury methylation and demethylation, as well as the net methylation rate, were thought to reflect the severity of the problem. Secondly, it was felt that the organic content of reservoir sediments could be used to indicate the potential for methylation.

2.3 Space

Defining the spatial extent and resolution of any problem is a critical step, since it determines the level of detail and places limits on what is to be considered.

The participants emphasized that the influence of mercury bioaccumulation could extend beyond the reservoir itself to downstream waters. This has been documented in the English-Wabigoon River in northern Ontario, where high mercury levels have been observed in waters downstream of the original source of mercury (Parks et al., 1980). Therefore, for the purposes of this project, the spatial horizon under consideration was the limit of measurable effects on indicators, particularly fish.

Table 2.2: Indicators.

1. Mercury content of (inorganic, methyl, dissolved, bound):

- fish
- waterfowl
- aquatic mammals
- humans
- water
- zooplankton
- benthos
- aquatic plants
- surface sediments
- flooded soils

2. Rate of mercury methylation and demethylation; net rate of methylmercury production

3. Organic content of the sediments

Within this horizon, it was useful to divide the area into functional zones expected to produce different indicator values:

- 1) the reservoir's watershed;
- 2) the reservoir, including:
 - a) water - epilimnion and hypolimnion;
 - b) sediment - active and inactive layers; and
 - c) flooded land - originally flooded area (where applicable), post-impoundment permanently flooded area, and drawdown zone; and
- 3) waters downstream of the reservoir.

2.4 Time

It has not yet been established how long it takes for elevated mercury levels in hydroelectric reservoirs to disappear naturally. Recovery times may vary between regions, or even for different reservoirs within a region. Therefore, it was agreed that the time horizon should be specified only as that required for fish mercury concentrations to return to a level consistent with pre-impoundment values (or uncontaminated reference area values). It was thought unlikely that this would extend beyond 50 years.

Having defined the time horizon, the group discussed the temporal resolution, or time step, over which indicators need to be sampled (from either a real system or a simulation model). Clearly, different indicators need to be sampled at different frequencies. For biota, particularly long-lived species, a resolution of less than one year would often be unnecessary. Conversely, consideration of sedimentation or erosion processes would require much more frequent iteration, particularly at the initiation of the work.

2.5 Submodel Definition

Having specified the actions and indicators essential to the mercury problem, as well as appropriate spatial and temporal limits, the conceptual model was divided into a number of subsystems. This division permits different subsystems of the mercury problem to be concurrently addressed by smaller groups of participants, rather than the whole group attempting to study the problem in its entirety.

The complexity of the issue made it difficult to divide the problem into subsystems. Three subgroups were finally delimited on the basis of the processes they encompassed:

- 1) site selection and reservoir construction;
- 2) physical, chemical and microbiological processes; and
- 3) pathways of mercury in biota.

The major pathways between these subsystems are illustrated in Figure 2.1.

2.6 Looking Outward

The purpose of the looking outward exercise is to define the pieces of information a particular system requires from all subsystems in order to predict how that subsystem's indicators will change over time. The product of this exercise is an interaction matrix, with the columns specifying what information a subsystem requires from each of the other subsystems listed on the rows (Table 2.3). The diagonals are not filled in since they represent the internal dynamics of each subsystem.

Together with Figure 2.1, the information transfers specified in Table 2.3 represent an initial overview of the system. In the subgroup discussions, it became clear that some information was

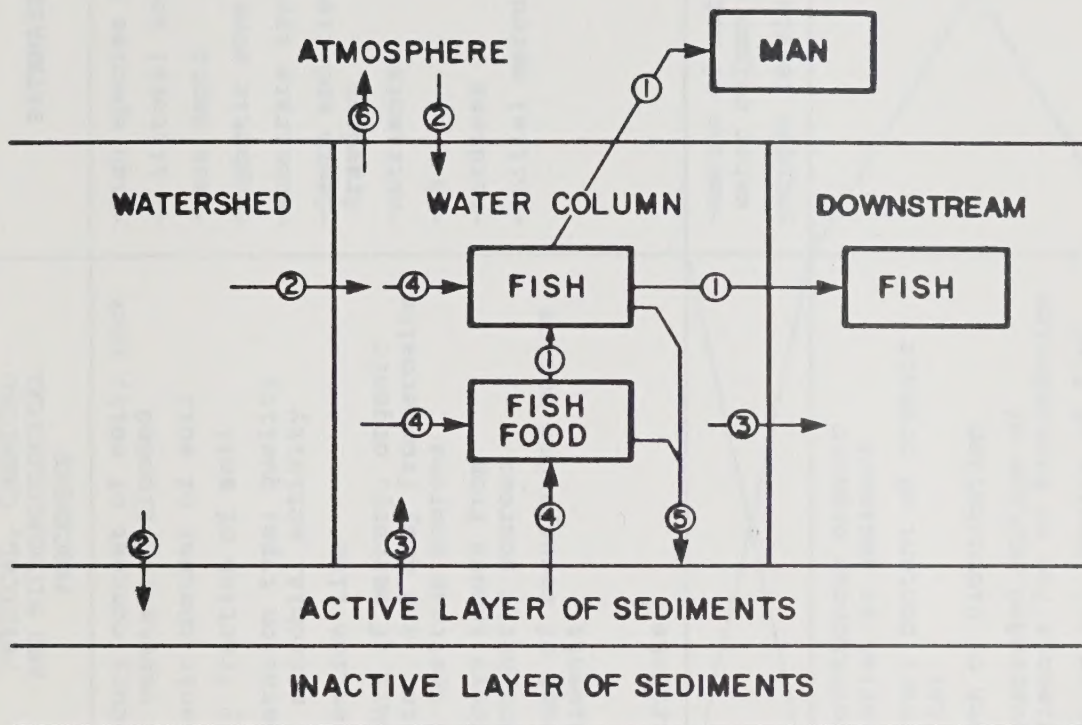


Figure 2.1: Simplified conceptual model of a theoretical reservoir, showing movement of mercury between ecosystem compartments. Numbers group transfers according to subgroup(s) responsible.

- 1 - processes internal to biota subgroup
- 2 - from site selection subgroup to physical/chemical/microbiological subgroup
- 3 - processes internal to physical/chemical/microbiological subgroup
- 4 - from physical/chemical/microbiological subgroup to biota subgroup
- 5 - from biota subgroup to physical/chemical/microbiological subgroup
- 6 - from physical/chemical/microbiological subgroup to site selection subgroup

Table 2.3: Looking outward matrix.

FROM	TO	SITE SELECTION AND RESERVOIR CREATION	PHYSICAL, CHEMICAL AND MICROBIOLOGICAL PROCESSES	PATHWAYS TO BIOTA
SITE SELECTION AND RESERVOIR CREATION			-mercury content of soil, rock and vegetation flooded -organic content of soil -clay fraction of soil -vegetation type; quality for microbial activity -retention time -inputs of mercury, organic matter, and clay from erosion and upstream sources -mercury inputs from atmospheric sources -amount of resuspended bottom sediments -pH -nutrients	-fish species present -% littoral zone -mean depth -euphotic zone depth -substrate type -depth and frequency of drawdown -nutrients -pH -hardness -initial mercury levels
	PHYSICAL, CHEMICAL AND MICROBIOLOGICAL PROCESSES			-amount of methylmercury in water column and sediments -oxygen levels
PATHWAYS TO BIOTA			-autochthonous organic material in sediment -mercury content of organic matter -depth of bioturbation -resuspended portion of sediments due to bioturbation -biomass and species of fish present	

superfluous, or could not be addressed with current technology. In other cases, it was recognized that more detailed information was necessary to produce accurate predictions of effect.

3.0 SUMMARY OF SUBGROUP DISCUSSIONS

The purpose of the subgroup discussions was to develop a conceptual model of the system, consisting of a set of linked hypotheses. Both the conceptual model and the hypotheses are described in Section 4. This section serves as both a background and supplement to Section 4. The background information consists of elaborations on the hypotheses; the supplementary information summarizes discussions which were relevant to the overall problem but were not easily assigned to any particular hypotheses.

3.1 Site Selection and Reservoir Creation Subgroup

The looking outward matrix demonstrates the overwhelming influence of reservoir site characteristics on mercury bioaccumulation. This led the subgroup to examine traditional reservoir planning considerations relative to those related to mercury.

Traditionally, mercury accumulation has not been considered during reservoir planning. The factors typically considered include:

- 1) amount of water the reservoir can hold;
- 2) topography of the area to be flooded;
- 3) present land use of area to be flooded;
- 4) length of necessary transmission line;
- 5) uses other than power production for reservoir (e.g., recreation, irrigation, commercial fishery, flood control); and
- 6) type of reservoir (e.g., run-of-the-river, storage, diversion).

Additional considerations which relate to the mercury perspective on the problem include:

- 1) retention time;
- 2) fluctuations in water levels due to drawdown;
- 3) characterization of bedrock and soils in area to be flooded;
- 4) characterization of vegetation in area to be flooded;
- 5) mercury inputs from atmosphere and nearby point sources; and
- 6) potential wave energy and depth.

The addition of sediments capable of providing a basis for methylation, and the processes whereby sediments would be added to the system (i.e., erosion) received considerable attention. The amount of sediment available was felt to be a function of the amount of land flooded; the nature of the area flooded (convoluted versus smooth topography); the increments of sediments introduced from the watershed, from erosion, and from sections of sediments breaking free of the bottom; and the losses of sediment at the reservoir outflow.

Resuspension of sediments, particularly clays, has been suggested as a means of binding mercury, thus precluding its entry into the food chain. Given the variation in effect from resuspension of different types of sediment, and the uncertainty associated with the potential benefits, there was agreement that this is not presently considered a viable mitigative action.

Erosion rates obviously play a role in determining the amount of organic material being introduced into a reservoir.

Factors affecting erosion rate include wave energy (based on fetch, basin depth, basin morphometry and nearshore slope), soil type, bank height, amount of overburden, and change in water level.

Erosion control is currently employed in some reservoirs, but not for reasons of preventing mercury-laden soils or organic matter from reaching the water. It was felt that the contribution of erosion to the mercury problem was insignificant in comparison to other site selection factors; therefore, it was considered unlikely that erosion control would be given priority as a mitigative strategy.

3.2 Physical, Chemical and Microbiological Processes Subgroup

The subgroup spent most of their time discussing the processes by which mercury moves through different compartments of the ecosystem, and how these processes affect both the success of proposed actions and the importance of different site parameters.

The actions discussed by the group included covering bottom sediments with "clean" clay (either directly or through resuspension of clay sediments within the reservoir), and a set of possible chemical additions (sulfate, lime, nutrients and selenium).

Covering bottom sediments with clean clay is intended to dilute the organic matter content of the sediments, neutralize existing sites for bacteria, and bind mercury in the sediment. Counter to expectations, clay additions may, in the short term, enhance methyl mercury production. In the long term, methyl mercury production should decrease, provided that shoreline erosion does not bring more organic matter into the sediments. In general, it seems that erosion rates are greater where banks have a high percentage of clay (e.g., South Indian Lake (S.I.L.)) than where the percentage is low (e.g., St. Maurice River reservoir in Quebec). This would imply that bank erosion is more likely to decrease than to increase methyl mercury production. However, since in most cases

only a small percentage of bottom sediments will be covered, increased erosion may not significantly change average sediment organic matter in either direction.

Most chemical additions were rejected as being infeasible. Sulfate additions can be used to precipitate mercury, but may only remove iron. Nutrient and lime additions were also not considered to be worthwhile. Nutrient additions could worsen the problem by increasing methylation rates, instead of diluting the pool of methyl mercury through a larger biomass of fish. Raising the pH via lime additions, so as to increase the proportion of dimethyl mercury (which is volatile and therefore leaves the system) was thought to only be practical for small reservoirs.

Selenium can both reduce the toxicity of mercury and decrease the amount of bioaccumulation occurring in the food web. It has been demonstrated that selenium additions do not affect rates of methylation, though effects on rates of demethylation are unknown. In general, the use of selenium to mitigate the mercury problem is promising. Major hurdles to be overcome include demonstrating that: Se consistently and significantly lowers rates of bioaccumulation; Se toxicity does not occur at the concentrations being considered; and the "safe" level of mercury contamination should depend on the ratio of [Se]:[Hg] as well as [Hg] in fish flesh. It was noted that the fish inspection service of the Department of Fisheries and Oceans has data on both Se and Hg concentrations in fish.

The subgroup discussed most of the site parameters listed in the looking outward matrix (Table 2.3). As much of this discussion is summarized in Section 4; only supplementary information is presented here. The mercury content of flooded soils, rock and vegetation was judged to be much less important than the organic content (BOD) of soil and vegetation. Studies at S.I.L. found no relationship between $[Hg]_{\text{soil}}$ and $[Hg]_{\text{fish}}$, but this result may be partially due to the low contrast in $[Hg]_{\text{soil}}$. The mercury content

of vegetation will be measured this summer at S.I.L. Mercury concentrations in tamarack, black spruce, lichens, and other vegetation types are listed in Fraser and Elcabetz (1978).

Water retention time was not thought to have much effect on $[Hg]_{\text{fish}}$, though it was recognized as an important parameter in determining the feasibility of a number of possible actions (e.g., using clay to cover bottom sediments, chemical additions, etc.). The S.I.L. study shows no difference in $[Hg]$ of resident fish between areas with low (5 days) and high (1.5 years) retention time. It was pointed out that equilibrium between water and sediments is reached fairly quickly. For retention time to lower $[Hg]_{\text{fish}}$, it must be less than the time to establish a sediment-water equilibrium. The position of a sub-basin (e.g., amount of flooded area upstream) is likely to be more important than its retention time.

The subgroup discussed the effect on mercury concentrations of significantly reducing the amount of fish biomass in the reservoir. Two different viewpoints emerged. The first hypothesis was that removal of fish would slow the cycling of mercury and gradually lower the concentration of mercury in fish food. An alternative hypothesis held that no changes would be observed in $[Hg]_{\text{fish food}}$ since removal of fish did not change the total pool of methyl mercury in the reservoir and in any case, the fraction of this pool contained in fish is extremely small.

The subgroup stressed the necessity for examining processes within the flooded area. Both the total land area and the per unit area change in methyl mercury production is much greater in the flooded zone than in the zone of the original water body.

3.3 Biota Subgroup

The biota subgroup discussed the uptake of methylmercury from the water column by various organisms and the subsequent food chain related transfers of mercury. In addition, factors affecting bioturbation rates and sedimentation of autochthonous organic matter were briefly discussed.

The concentration of methylmercury (CH_3Hg) in fish at any point in time can be expressed as a simple difference equation relating the balance between uptake and loss. That is:

$$\text{Hg}(t+1) = \text{Hg}(t) + \text{uptake} - \text{losses}$$

where,

$\text{Hg}(t+1)$ = the amount of mercury present in the fish
at time $t+1$;

$\text{Hg}(t)$ = the amount present at time t ;

uptake = the amount taken up during one unit of time;
and

losses = the amount lost during one unit of time.

During the discussion it was pointed out that while methylmercury is the species of greatest concern for human health, most studies report the concentration of total mercury (all forms). Typically, methylmercury represents 85% of the total mercury concentration and in our discussions we made no attempt to distinguish between the different species. Furthermore, we noted that most studies to date have not reported specifically on rates of uptake but rather on the final "equilibrium" concentrations of mercury in fish and how these appear to be influenced by various factors.

During the discussion it was noted that the rate of loss of mercury from fish may be addressed experimentally by holding contaminated fish in clean environmental conditions and monitoring the decline in mercury concentrations through time. Previous studies have expressed this function in terms of a "half-life" for mercury loss. Specifically, Norstrom et al. (1976) have noted that losses may be described as an exponential function of the body weight of fish, independent of such factors as metabolic rate.

In general, mercury may be taken up by fish from the water across any of the major body interfaces; gills, skin or gut. While considerable debate has been devoted to the question of whether the predominant pathway is through the gut (food sources) or gills, substantial uncertainty remains. In either case, several factors are known or suspected of limiting the rate of uptake (final concentration). During our discussions, it was apparent that these factors are common to either pathway and suggest that substantial effort to resolve the mechanistic details is not warranted.

Factors suggested as influencing the concentration of mercury in fish included [Hg] in the source (water or food), temperature, pH, weight (age), [Ca], [Se], metabolic rate, and efficiency of uptake. Increasing amounts of calcium or selenium tend to reduce the final concentration of Hg in fish, through inhibition of Hg uptake (either at the gill surface or across the gut wall). Higher concentrations of mercury have been found to be associated with elevated temperature or metabolic rate. While higher concentrations are also found in heavier/older fish, this may simply be the result of uptake over a longer time interval, or of increases in uptake rates associated with factors which accelerate growth (e.g., temperature, food availability/consumption, metabolic efficiency).

3.3.2 Bioturbation

Our discussions about bioturbation were concerned with how the rate of bioturbation could be predicted from relatively simple information about a site. Although the detailed mechanisms of bioturbation can be quite complex, our primary concern was at a more general level.

Within the context of the workshop, the significance of bioturbation lies in the mobilization of mercury through biological mixing of sediments. During the initial plenary session, both the total amount of sediment mixed and the depth of mixing were suggested as variables which would affect the mercury available for methylation and subsequent uptake by fish.

The principal factors identified during our discussions were the sediment type (e.g., silt, sand, clay, rock), and the type of benthic community. Sediment type influences bioturbation rates in two ways. Physical characteristics of the sediment particle size and compaction may act to limit the amount of mixing possible. The organic content of the sediment influences not only the biomass of benthos, but also the benthic activity and hence the bioturbation rate. The most important feature of the community type is whether it is dominated by epifauna or infauna. While the species composition is also recognized as a determinant of bioturbation rates, this level of detail was not considered important for our purposes.

4.0 HYPOTHESES OF EFFECT

Based on the subgroup discussions during day 2 of the workshop, the processes of methylmercury production and bioaccumulation were summarized in the form of a conceptual model (Figures 4.1 and 4.2) and hypotheses (see following pages). The diagrams and hypotheses provided a basis of discussion for further subgroup meetings on day 3, with a view towards developing a research plan.

Subgroups were then formed to subject each hypothesis to the questions illustrated in Figure 4.3. Hypotheses 1 to 11 were evaluated first, since they appeared to be the hypotheses that could most feasibly be addressed within this project.

During the discussions of hypotheses 1 to 11, it became evident that though the problem can be conceptualized into separate processes, it is generally extremely difficult to examine these separate processes in the field. Microbial activity and methylation rates, for example, are extremely variable both spatially and temporally. This greatly impedes attempts to demonstrate each linkage in the cause-effect chain from increased organic matter to increased concentrations of mercury in fish. Experiments conducted by the Freshwater Institute have shown that fish mercury concentrations consistently integrate (and reduce) the fluctuations inherent in lower trophic levels' activity. Therefore, rather than proceeding to evaluate hypotheses 12 to 17, the subgroups reassembled and developed a simpler conceptual model (Figure 4.4), which excluded the system components that link site factors to mercury concentrations in fish. The participants then "walked around the wheel" of Figure 4.4, assessing each parameter in terms of existing data and the needs for further research. The group's conclusions are presented in Section 5.

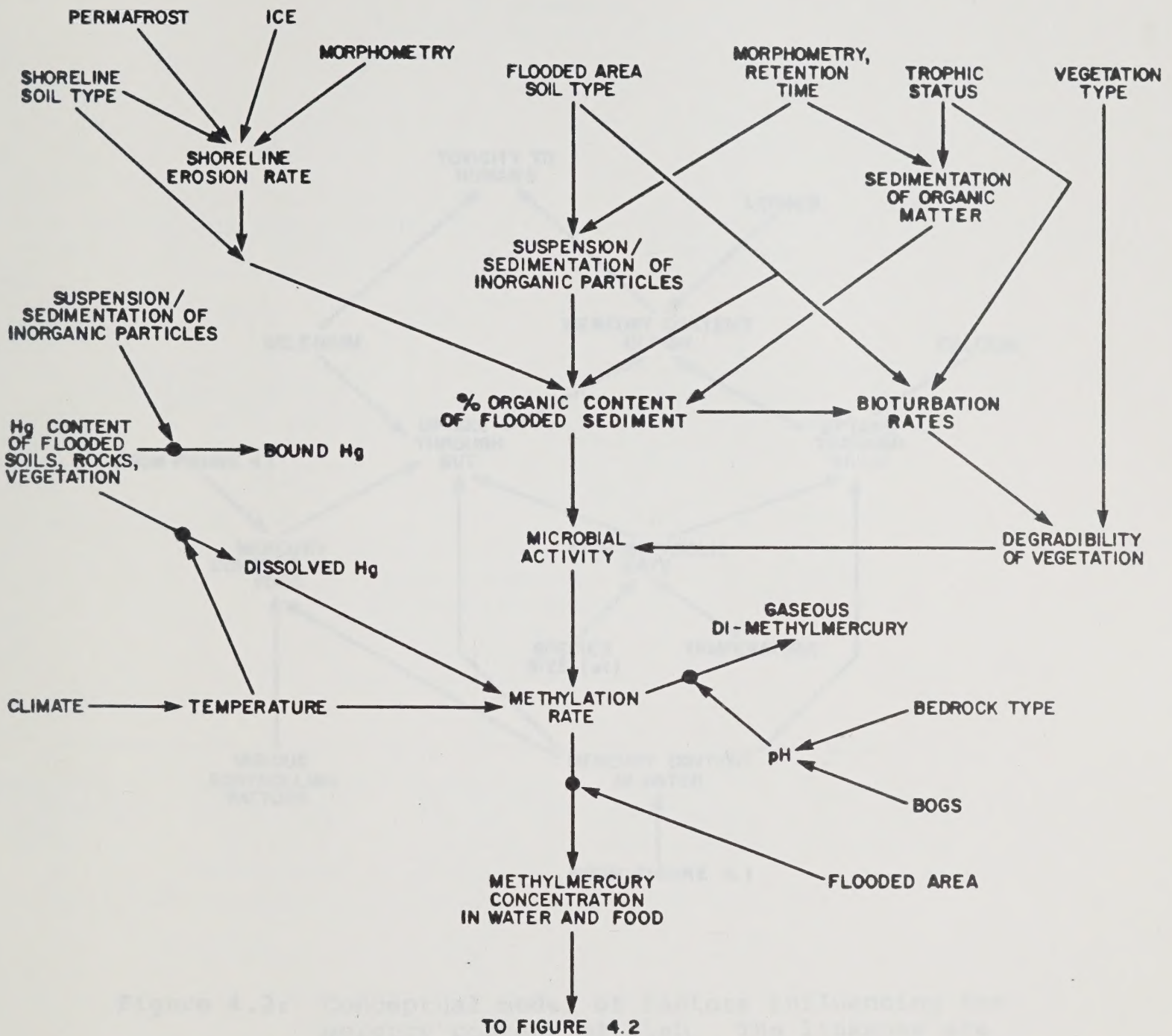


Figure 4.1: Conceptual model of factors influencing the concentration of methylmercury in water and food. The linkages are described and evaluated on the following pages.

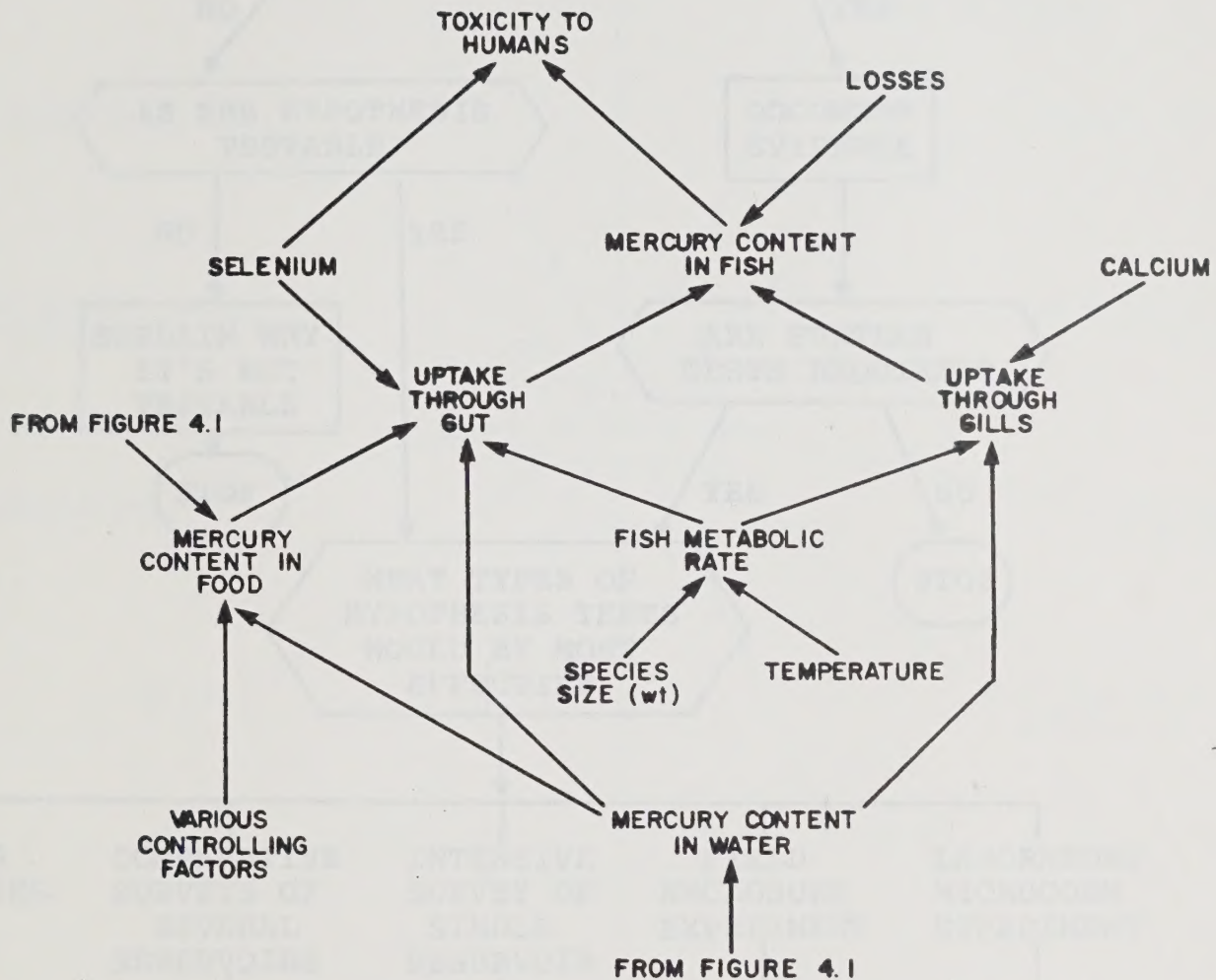


Figure 4.2: Conceptual model of factors influencing the mercury content of fish. The linkages are described on the following pages, but were not formally evaluated at the workshop.

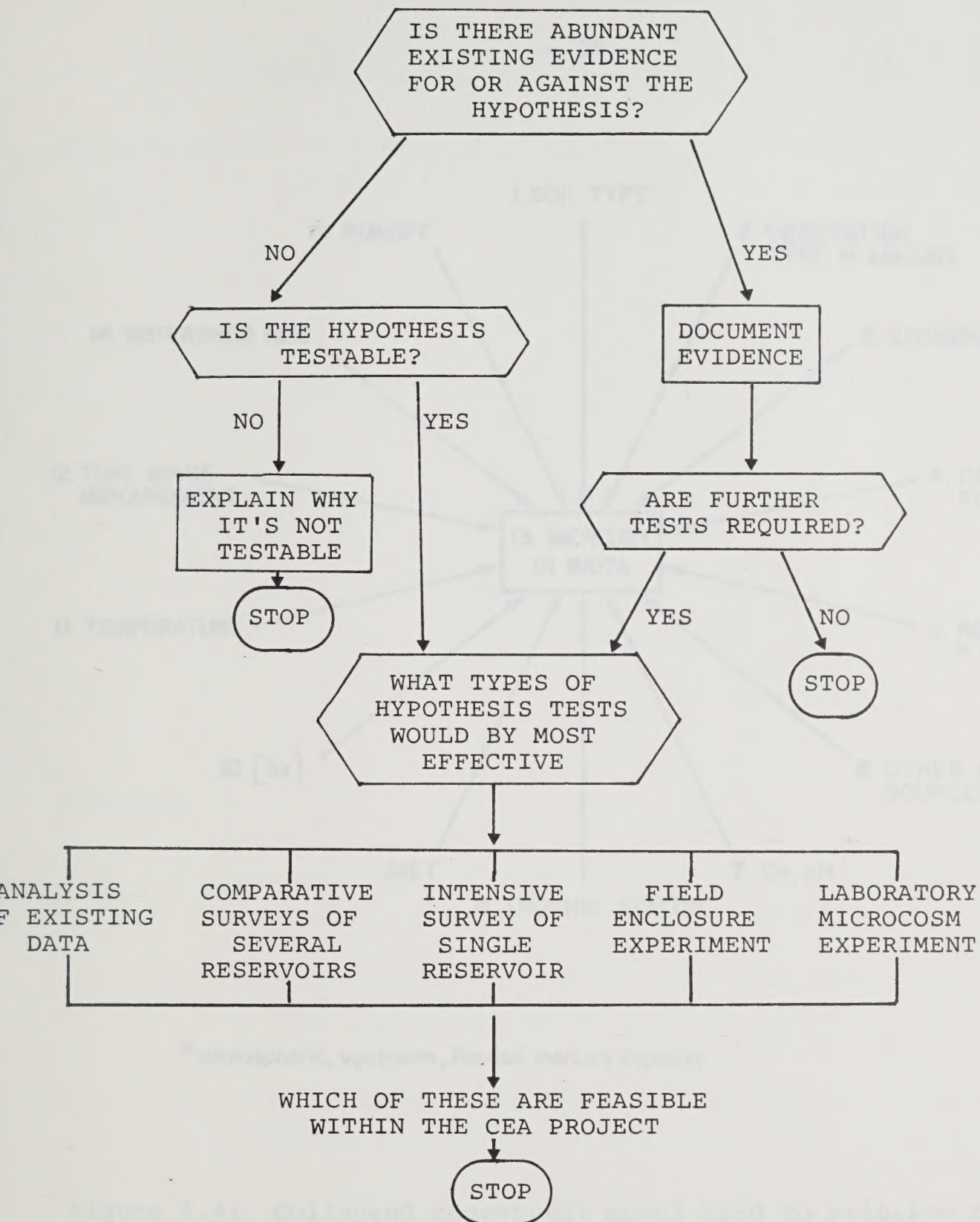
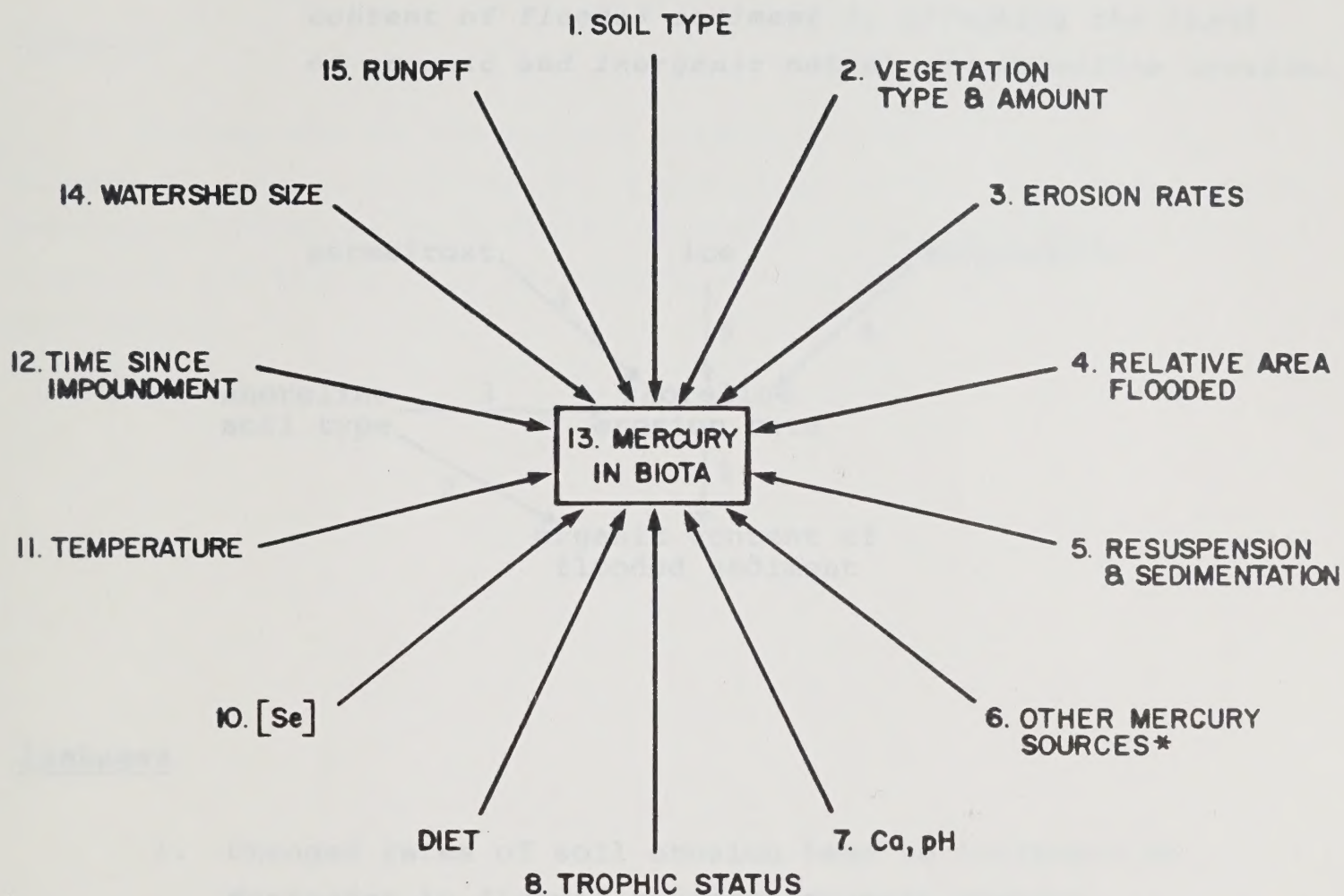


Figure 4.3: Questions used to evaluate appropriateness of performing research to test specific hypotheses.

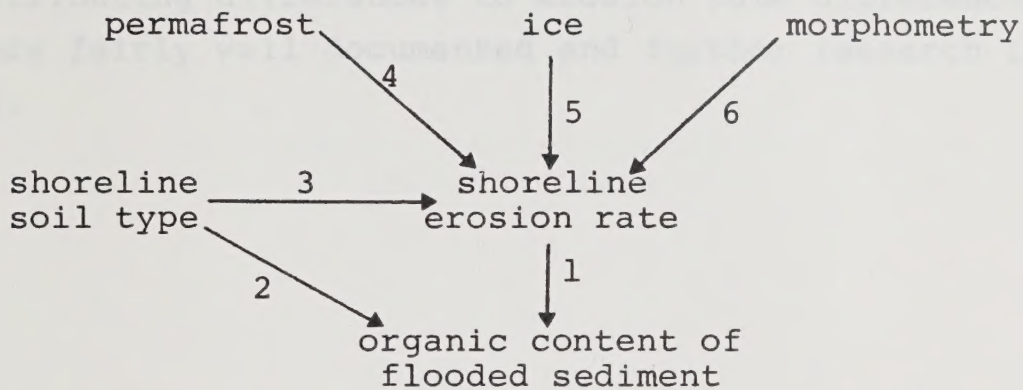


* atmospheric, upstream, flooded mercury deposits

Figure 4.4: Collapsed conceptual model used to prioritize research opportunities. Numbers refer to Table 5.1.

4.1 Description of Hypotheses and Summary of Participants' Comments

Hypothesis 1: Site characteristics influence the percent organic content of flooded sediment by affecting the input of organic and inorganic matter via shoreline erosion.



Linkages

1. Changed rates of soil erosion lead to increases or decreases in flooded sediment organic content.
2. Organic content of eroded soils determines the effect of erosion on change in sediment organic content.
3. The presence of erodable shoreline soils leads to elevated rates of soil erosion.
4. Presence of permafrost leads to increased rates of shoreline erosion.
5. Scouring effects of ice lead to increased shoreline erosion rates.

6. By affecting the amount and direction of wave energy, morphometry influences the amount of shoreline erosion rates.

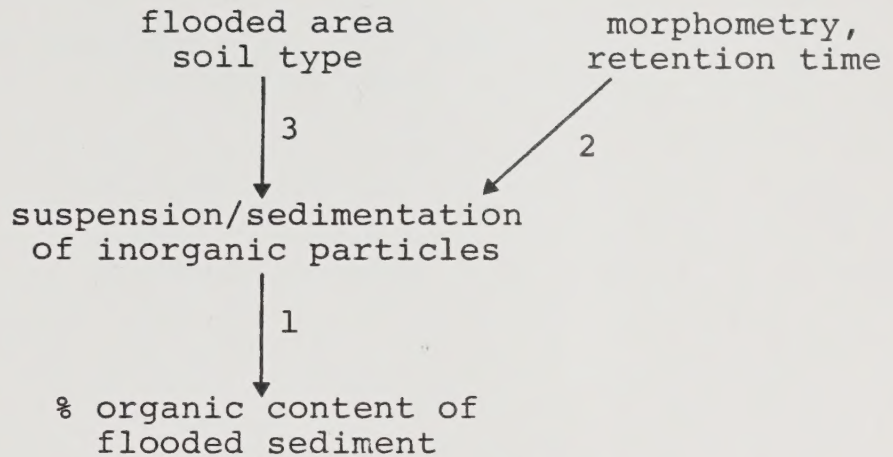
Comments

Changes due to erosion are likely very small compared to effects of initial flooding, and variability between reservoirs would preclude attributing differences to erosion rate differences. Erosion processes are fairly well documented and further research is unnecessary.

References

1. Resuspension (and sedimentation) of inorganic particles will increase (and decrease) the percent organic content of flooded sediments.
2. Reservoir morphometry and retention time will affect the energy available for resuspension and sedimentation of inorganic particles.
3. The particle size composition of flooded soils will affect the rate of resuspension and sedimentation of inorganic particles.

Hypothesis 2: Site characteristics influence the percent organic content of flooded sediments by affecting resuspension and sedimentation of inorganic particles.

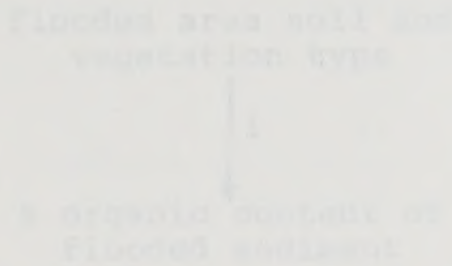


Linkages

1. Resuspension (and sedimentation) of inorganic particles will increase (and decrease) the percent organic content of flooded sediment.
2. Reservoir morphometry and retention times will affect the energy available for resuspension (or sedimentation) of inorganic materials.
3. The particle size composition of flooded soils determines the availability of inorganic material to be resuspended.

Comments

Resuspension and sedimentation occur in reservoirs to varying degrees, but there is not much you can do about it. Therefore, the research money is better spent elsewhere.



Conclusions

1. As stated above.

Recommendations

The group concluded that this hypothesis was true and that it would be worthwhile to take it one step further: to study the effect of vegetation on the organic content of flooded sediment. This could be done by:

- 1) Analysis of existing data;
- 2) Comparative surveys of natural reservoirs; and
- 3) Intensive survey of a single reservoir.

Comparisons of cleared and non-cleared reservoirs could be made to study the effect of vegetation on the organic content of the flooded sediment.

Hypothesis 3: The percent organic content of flooded sediment is strongly influenced by the composition of the upper soil horizons flooded and the amount and type of flooded vegetation.

flooded area soil and
vegetation type

↓
1

% organic content of
flooded sediment

Linkages

1. As stated above.

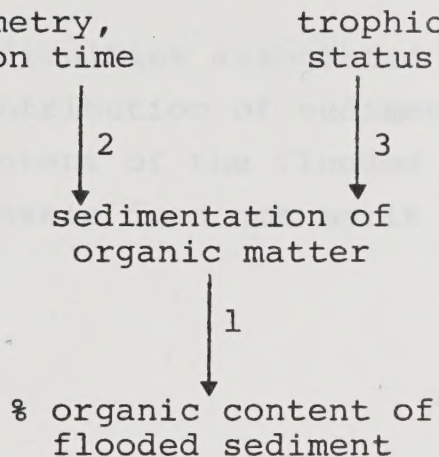
Comments

The group concluded that this hypothesis was true, but that it would be worthwhile to take it one step further; i.e., what influence does the flooded soil have on the $[Hg]_{\text{fish}}$. This could be addressed by:

- 1) analysis of existing data;
- 2) comparative surveys of several reservoirs; and
- 3) intensive survey of a single reservoir.

Comparisons of cleared and non-cleared reservoirs could be used to study the effect of vegetation on the organic content of the flooded sediment.

Hypothesis 4: Site characteristics affect the percent organic content of flooded sediments by influencing the sedimentation of organic matter.



Linkages

1. Sedimentation of organic matter will lead to increased percent organic content of flooded soils.
2. Reservoir morphometry and retention times will influence the rates of sedimentation of organic matter.
3. Reservoirs with a higher trophic status will tend to have greater rates of sedimentation of organic matter.

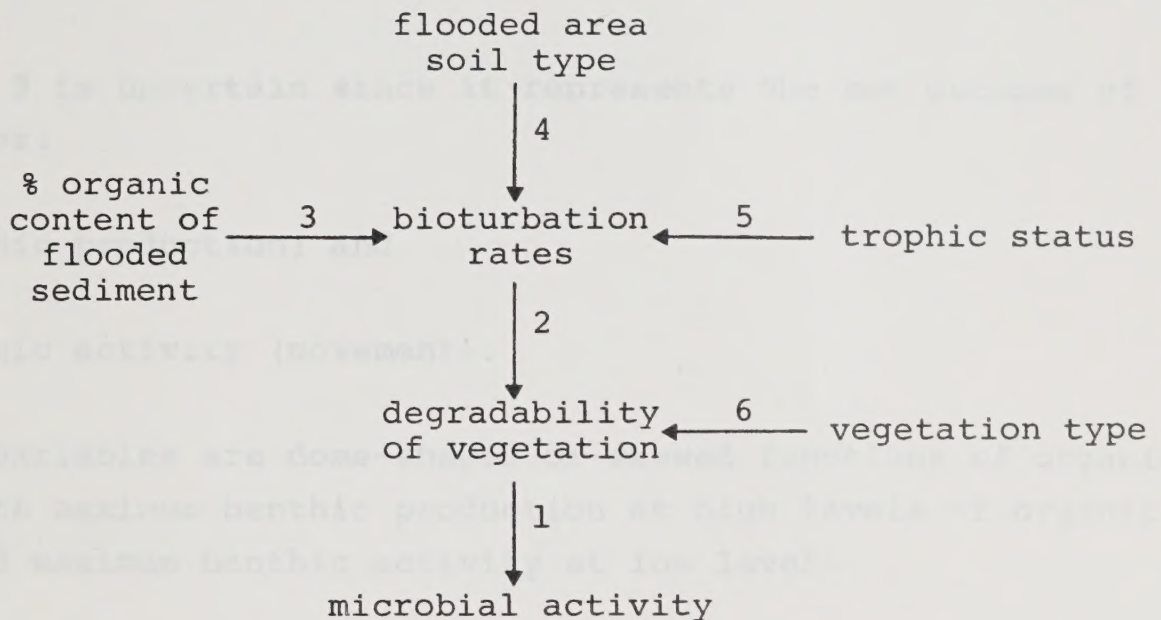
Comments

Considerations of sedimentation of organic matter are not as important as the original characteristics of the soil flooded. It was not clear which way the site characteristics would influence the sedimentation processes (increase or decrease). The time horizon for any research related to this would be beyond the scope

of this project. Some information might be obtained by comparing the predictions of existing sedimentation models used by utilities to predict the useful life span of a reservoir with analysis of the organic content of bottom core samples. This would be limited by the resolution of the core sampling analysis (approximately 5 years) and would be feasible only for older reservoirs.

In view of the difficulties associated with testing this hypothesis and the low contribution of sedimentation of organic matter relative to the content of the flooded soils, it was concluded that this hypothesis does not merit testing.

Hypothesis 5: Site characteristics influence rates of microbial activity, both through affects on bioturbation and through the composition of vegetation.



Linkages

1. Increased degradability of vegetation will lead to increased microbial activity.
2. Increased rates of bioturbation will increase the degradability of vegetation.
3. Increased percent organic content of flooded sediments, by stimulating increased benthic production, may lead to increased overall bioturbation rates.
4. Greater bioturbation rates will occur in flooded soils with smaller average particle sizes.

5. Reservoirs with a higher trophic status will tend to have greater bioturbation rates.
6. The composition of the vegetation in the flooded area will affect its degradability.

Comments

Link 3 is uncertain since it represents the net outcome of two processes:

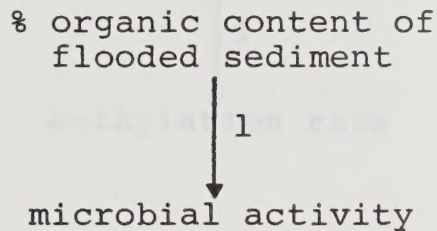
- 1) benthic production; and
- 2) benthic activity (movement).

Both these variables are dome-shaped or skewed functions of organic content, with maximum benthic production at high levels of organic content, and maximum benthic activity at low levels.

For all other links, the statements were accepted as known or having some supporting literature now. With regard to testing, two approaches were recommended:

- 1) further analysis of existing literature/data; and
- 2) microcosm and/or enclosure experiments to address 3, however, resolving the detailed mechanisms related to bioturbation was considered to be a low priority because of the restricted potential for mitigation. (Note that mitigation through sediment modification to inhibit bioturbation (e.g., capping) would not likely be independent of similar activities related to soil type).

Hypothesis 6: Increased amount and quality of organic content of the flooded sediments will lead to increased microbial activity.



Linkages

1. As stated above.

Comments

The best measure of the organic content of sediments is its degradability, as measured by microbial activity or BOD. Therefore, the hypothesis is tantological. However, it would be useful to classify soils surrounding existing reservoirs according to their BOD content, using laboratory incubations of different soils. The Freshwater Institute will be doing some of these tests this summer on Stevens, Reindeer, Cedar and Sipiwesk Lakes. Existing information: Todd Jackson (Environment Canada), Hynes (University of Waterloo), past surveys on Notigi and S.I.L. reservoirs, agricultural and forestry scientists.

Hypothesis 7: Increased microbial activity leads to increased methylation rates.

microbial activity

↓
1

methylation rate

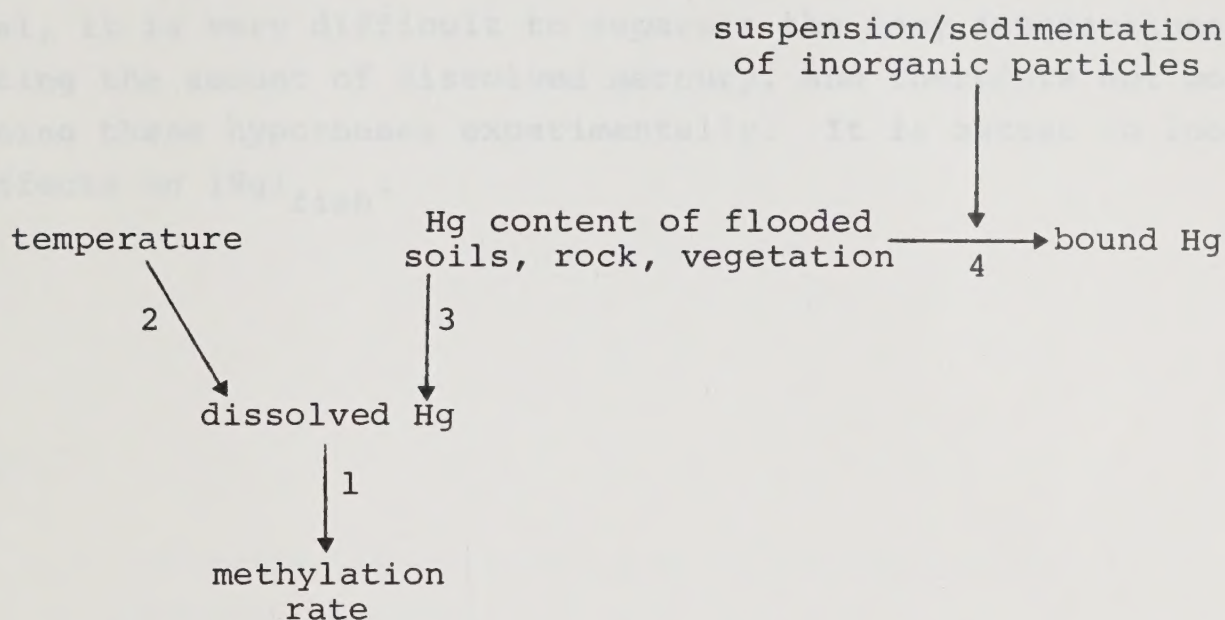
Linkages

1. As stated above.

Comments

Existing evidence from English Wabigoon is sufficient to validate the hypothesis; further testing not warranted. Proper testing requires much effort as methylation rates show considerable temporal variation due to changes in bacterial community and temperature. Also, much microbial activity is unrelated to methylation.

Hypothesis 8: Resuspension and sedimentation of inorganic particles, the mercury content of the flooded area, and temperature will influence the amount of dissolved mercury available for methylation.



Linkages

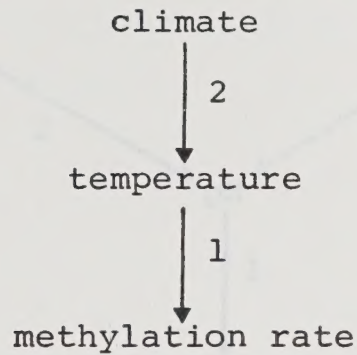
1. Increased levels of dissolved mercury will permit increased methylation rates.
2. Elevated water temperatures lead to increased rates of dissolution of mercury from flooded soils, rock and vegetation.
3. The mercury content of flooded soils, rock and vegetation determines the potential level of dissolved mercury.

4. Resuspension and sedimentation of inorganic particles binds mercury, reducing the amount of mercury dissolved from flooded soils, rock and vegetation.

Comments

The mercury content of flooded soils, rock and vegetation is never limiting; other factors tend to be more limiting. In general, it is very difficult to separate the many interactions affecting the amount of dissolved mercury, and therefore not worth examining these hypotheses experimentally. It is better to look for affects on $[Hg]_{\text{fish}}$.

Hypothesis 9: Climate influences the rate of methylation of mercury.



Linkages

1. Increased temperature leads to increased mercury methylation rates.
2. The climate of the site influences the temperature regime within the reservoir.

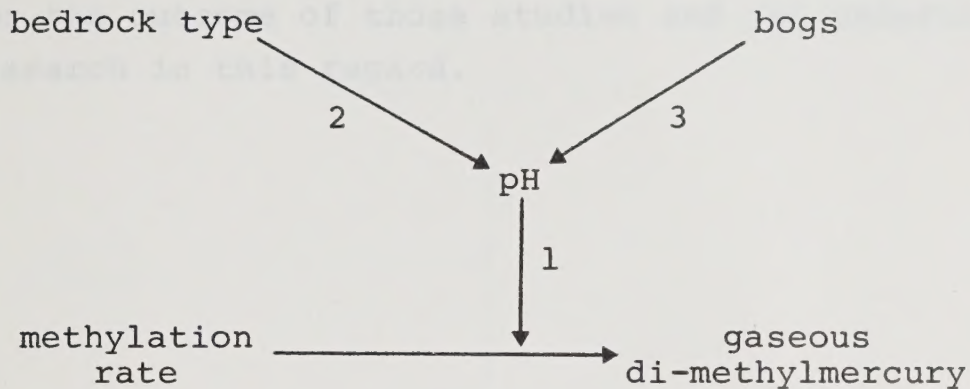
Comments

Both methylation and demethylation rates increase with temperature, so that there may be no net change in the [Hg] in water and fish food. The hypothesis is not worth testing.

Comments

The volatilization of di-methylmercury is well known but the conversion between these two forms under in-situ environmental conditions has not been verified experimentally. The theory of this conversion has been worked out but does not consider the possible effects of other chemical species in the natural environment.

Hypothesis 10: Site characteristics will affect reservoir pH, influencing the proportion of mono-methylmercury converted to di-methylmercury.



Linkages

1. Elevated reservoir pH leads to greater rates of conversion of mono-methylmercury to di-methylmercury, which volatilizes to the atmosphere.
2. Bedrock characteristics will affect reservoir pH due to the presence or absence of acid bearing or acid buffering rocks.
3. The presence of humic bogs in the area to be flooded will lead to decreased reservoir pH.

Comments

The volatilization of di-methylmercury is well known but the conversion between these two forms under in-situ environmental conditions has not been verified experimentally. The theory of this conversion has been worked out but does not consider the possible effects of other chemical species in the natural environment.

Experimental verification could be technically very difficult. Furthermore, the significance of the hypothesis is dependent upon the range of reservoir pH and would not be expected to contribute to elevated concentrations of mercury above pH 5.5. This problem is also of concern to studies related to acid rain and is being actively pursued in that context. It was recommended that this project monitor the outcome of those studies and not undertake independent research in this regard.



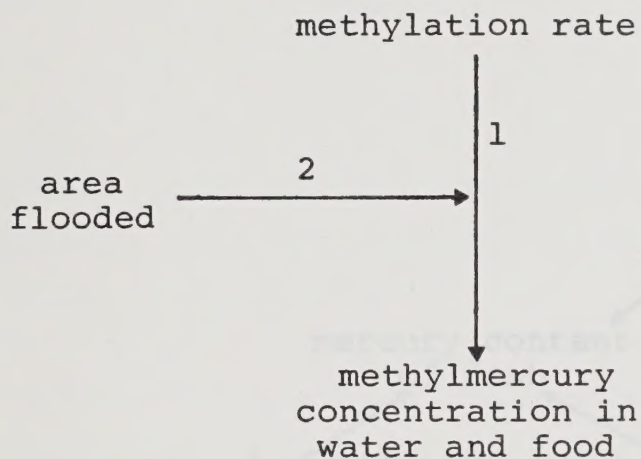
Discussion

1 and 2. As stated above.

Conclusions

This is a potentially important hypothesis, yet there is no current agreement on whether or not it is true. Studies of the hypothesis will require an understanding of the relationship between pH and mercury concentration in water and food. It is hoped that this project will contribute to the understanding of this relationship. It is also hoped that this project will contribute to the understanding of the relationship between pH and mercury concentration in water and food.

Hypothesis 11: Rates of methylation in the flooded area and the total or relative area flooded largely determine the concentration of methylmercury in water and fish food.



Linkages

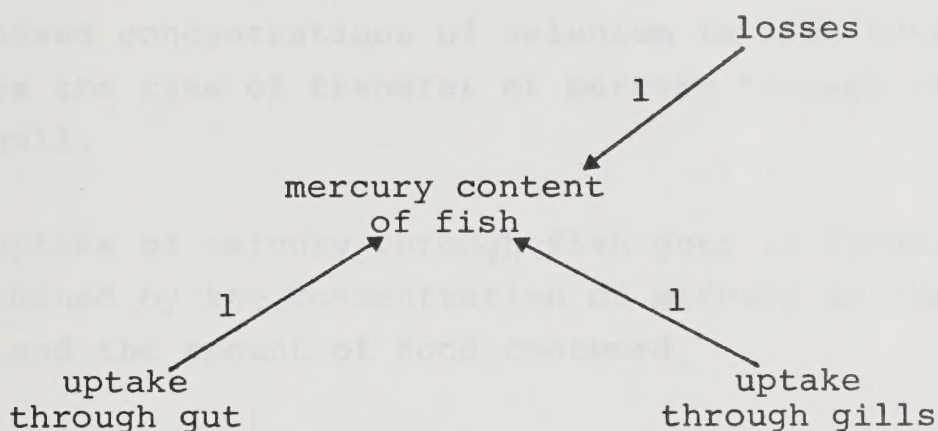
1 and 2. As stated above.

Comments

This is a potentially important hypothesis, yet there is no current agreement on whether or not it is true. Studies of the Churchill River diversion do support the hypothesis (Bodaly et al., 1984), and it should be tested in other areas of Canada. If pre-impoundment data does not exist, it may be possible to sample nearby water bodies to approximate historical values.

Hypotheses 12 to 17 were not formally evaluated at the workshop (see text for explanation).

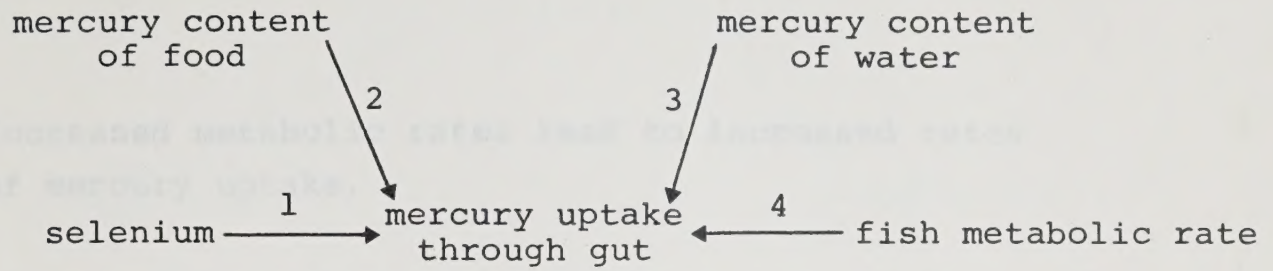
Hypothesis 12: Mercury concentrations in fish are increased by uptake of methylmercury through the gills and gut. Offsetting losses occur as an inverse exponential function of fish weight.



Linkages

1. As stated above.

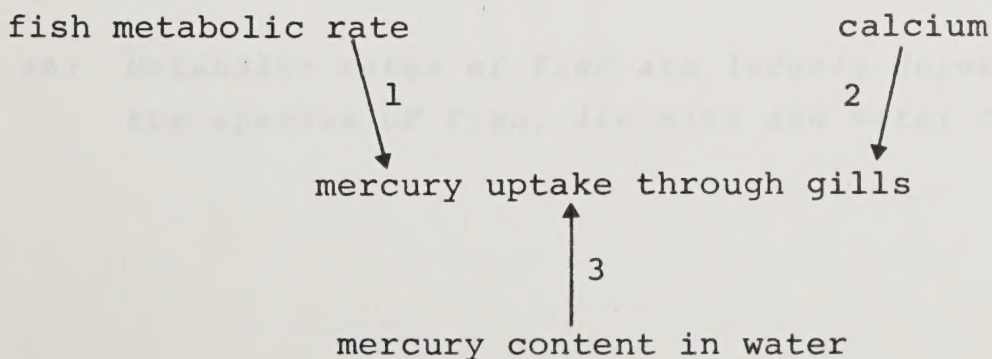
Hypothesis 13: The rate of mercury uptake through fish guts is affected by mercury concentrations in fish food (and also in water), fish metabolic rates and gut selenium concentrations.



Linkages

1. Increased concentrations of selenium in fish guts reduce the rate of transfer of mercury through the gut wall.
2. The uptake of mercury through fish guts is largely determined by the concentration of mercury in the food and the amount of food consumed.
3. The uptake of mercury through fish guts is partially determined by the concentration of mercury in water.
4. Increased metabolic rates lead to increased rates of mercury uptake.

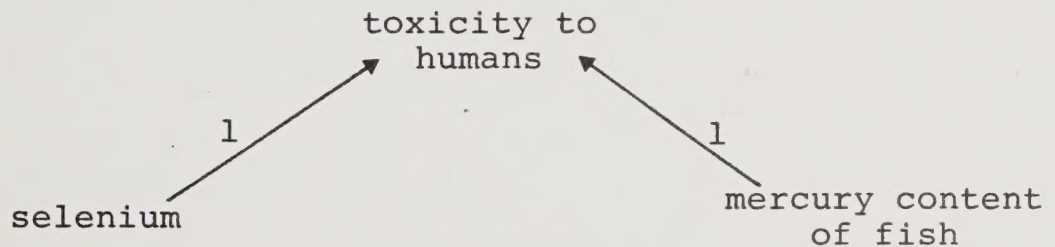
Hypothesis 14: The rate of mercury uptake through fish gills is affected by the mercury content of the water, fish metabolic rates, and calcium concentrations.



Linkages

1. Increased metabolic rates lead to increased rates of mercury uptake.
2. Increased concentrations of calcium lead to decreased uptake of methylmercury across the gills.
3. Uptake of mercury across fish gills is largely determined by the concentration of methylmercury in water.

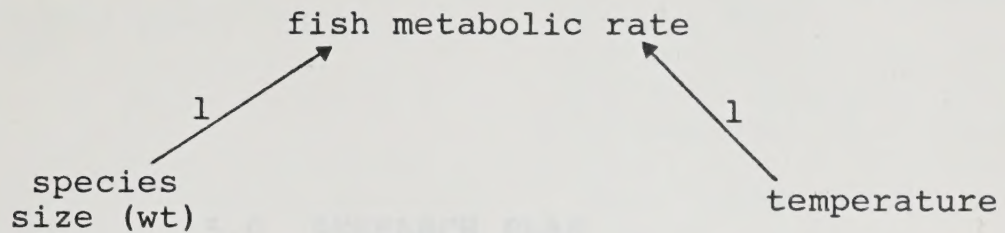
Hypothesis 15: The toxicity of mercury to humans is reduced by elevated selenium concentrations within the human body, either as a result of fish selenium concentrations or direct ingestion of selenium.



Linkages

1. As stated above.

Hypothesis 16: Metabolic rates of fish are largely dependent upon the species of fish, its size and water temperature.



Linkages

1. As stated above.

Hypothesis 17: The relationship between methylmercury in water and the amount of mercury in fish food is controlled by various factors, similar to those affecting fish uptake (e.g., calcium, temperature, metabolism, etc.).

[See Hypotheses 12, 13, 14 and 16.]

5.0 RESEARCH PLAN

5.1 Collection of Existing Data

It was evident from discussions on the final day of the workshop that the first priority should be to compile the existing data on as many Canadian reservoirs as possible. Data on reservoir site parameters (soils, geology, vegetation, bathymetric characteristics, etc.) should be used as independent variables in an attempt to explain the observed variation in fish mercury concentrations.

Table 1 provides a summary of the information needs identified during the mercury workshop. Data on these parameters will be collected from the listed sources over the next month. Much of the published information has already been assembled through the literature review and survey of current information conducted in March, 1984 as part of this study.

5.2 Analysis of Existing Data

5.2.1 Screening and Standardization

The data set will first be screened to remove those reservoirs with point sources of mercury pollution in their watersheds (e.g., chlor-alkali plants). The second step is to compare the methods used to measure the site parameters. If possible, all measurements will be converted to a standard method. However, it will likely be necessary to divide the data set for each parameter into several classes, based on the methods used. Third, we will attempt to standardize the data on fish mercury concentrations. Our approach is to choose a common species and age (or length) of fish (e.g., 8 year old whitefish), and using the best data sets available (reservoirs in which many species and ages of fish have been measured), determine

Table 5.1: Information needs identified at the mercury workshop.

FACTOR	UNITS	CONTACTS (SOURCES)
soil type	% flooded area of each soil type (from soil maps - define soil types)	Geological Survey of Canada/ forestry maps contact agricultural, forestry, microbial scientists at Guelph, UBC Environmental Impact Studies (EISs)
vegetation type & amount	% area by coniferous, deciduous, agricultural	pursue categorization with above contacts timber maps; pre-reservoir aerial photos (for a small # of reservoirs)
erosion rates	measurements from more recent reservoirs, or calculate erosion using fetch(km) and basin depth (m) soil type (categories) particle/grain size wind conditions (categories)	Greg McCullough (help to define categories)
relative area flooded	area and volume (or mean depth) for the original water body, the permanently flooded area, and the drawdown zone, by basin where applicable	Hydro utilities reservoir atlas (for volumes) CEA - Kingsley (for inventory of reservoirs)
resuspension & sedimentation	turbidity, secchi disc, TSS or use models incorporating mean depth, total area, annual distribution of wind speeds (wind rose), and the length & direction of the major axis of the reservoir	Geological Survey of Canada, CCIW
other mercury sources	presence/absence	Hydro companies provincial environmental agencies
Ca, pH	mg/l (Ca)	Hydro companies post-impoundment surveys -environment ministries -NAQUADAT data set
trophic status	total phosphorus (ug/l); chlorophyll a (ug/l); TDS (mg/l); MEI	same as for #7
diet	what type of fish are present - piscivorous, planktivorous, benthivorous fish stomach analysis	Hydro companies post-impoundment surveys -environment ministries
Se	relative concentrations in soils	selenium map for Canada Lorne Fisher Dept. Agric., Agassiz Marg Taylor, NRCC
temperature	degree days (annual and growing season)	Environment Canada data on local weather stations Agriculture Canada reports, maps

.../cont'd.

Table 5.1 (cont'd.):

FACTOR	UNITS	CONTACTS (SOURCES)
2. time since impoundment	years	Hydro companies
3. mercury in biota	ppm; data disaggregated by spp, length, and age individual observations (or mean and standard deviation) method of analysis when sampled (year, season) where in reservoir	reservoir studies by utilities, environment ministries DFO commercial fish data other water body surveys (which include reservoirs)
14. watershed size	ha	topographic maps utilities
15. runoff	mm	Hydrological Atlas

a set of transformation curves. We hope the curve formed by the ratio of two species' [Hg]-length curves will be similar across all reservoirs, even if fish mercury concentrations differ widely.

5.2.2 Data Base

Since most reservoirs will be missing values for several parameters, it doesn't make sense to create a data file with spaces for all parameters for each reservoir. Instead, each reservoir record will contain the name of the reservoir followed by as many parameter codes and values as exist for that reservoir. This "reservoir file" will act as a master file from which separate "parameter files" may be extracted to perform particular analyses. The data will be entered into ESSA's Spectrix computer and reformatted into separate files for particular statistical analyses. Some analyses will be performed on the Spectrix; for more sophisticated analyses, we'll use the MIDAS statistical system available at the University of Alberta, where ESSA has a computer account.

5.2.3 Data Analysis

Though it would be interesting to perform multivariate data analysis on the independent variables, using fish mercury concentration as the dependent variable, it seems likely that problems with missing data will shrink both the number of parameters that can be included and the sample size (i.e., number of reservoirs). However, if sample sizes and missing data permit, we would try to determine the ability of the independent variables to predict fish mercury concentrations in reservoirs (i.e., multiple regression with and without factor analysis; canonical correlations if there is more than one dependent variable), or to discriminate between reservoirs which have different "classes" of fish mercury concentrations (i.e., discriminant analysis).

Probably the data set will lend itself more to analyses of variance, testing the importance of only a few parameters (e.g., 1 - 3) at a time. Naturally, the effects on $[Hg]_{\text{fish}}$ of the parameters not included in the analysis will make it more difficult to find a significant effect. Tests of some hypotheses will be greatly facilitated if we can find data sets for which most of the parameter values are constant (e.g., a series of reservoirs with the same soil and vegetation type, but different percent area flooded). In some cases, the analysis will need to be purely qualitative because of data limitations.

If it appears from our initial review of the data that a little more field sampling (e.g., to measure turbidity, pH, Ca, fish $[Hg]$ in a few reservoirs) could greatly improve the data set, we may do so. If the data analysis later reveals particular parameters to be extremely important, we may consider slightly altering experimental designs to test out different site selection/mitigation hypotheses. However, since we will not be able to complete the data analysis before the first experiment starts, only later experiments can be modified.

5.3 Experimental Approaches and Issues to be Resolved

Based on the workshop discussions, the questions most amenable to experimental investigation are those concerned with the influence of preflooding soil type and/or vegetation type on the subsequent concentration of methylmercury in fish.

The primary thrust of the suggested experiments would be to determine whether it is possible to correlate general characteristics of preflood soil/vegetation (e.g., BOD) with subsequent post-flood levels of mercury in fish. In the event this proved feasible, the techniques developed could help provide a diagnostic tool for site selection and might also prove useful in helping to assess the potential of proposed mitigative measures, without conducting "whole reservoir" experiments.

5.3.1 Research Questions

The following list of research questions is intended to suggest the kinds of concerns which might be addressed. There is an inherent hierarchy in that questions pertaining to the examination of mitigative techniques are clearly dependent upon the demonstration/validation that a general measure such as BOD may serve as an indicator of post-flood mercury concentrations in fish. Aside from this consideration, the order of the questions is not intended to imply any priority. The questions are:

- 1(a). To what extent is $[Hg]_{\text{fish}}$ determined by the type of flooded soil?
- 1(b). How much difference is there between different soil types in their potential for reducing $[Hg]_{\text{fish}}$ (after flooding) via erosion, Hg-binding and sedimentation?
2. To what extent is $[Hg]_{\text{fish}}$ determined by the type of flooded vegetation?
3. Are there synergistic effects from combinations of soil and vegetation which can act either to increase or to decrease $[Hg]_{\text{fish}}$?
4. To what extent is $[Hg]_{\text{fish}}$ determined by the type of microbial community in the reservoir? (i.e., Are vegetation/soil both a necessary and sufficient condition to produce elevated levels of Hg in fish?)
5. What changes in $[Hg]_{\text{fish}}$ might be anticipated as a result of preflooding treatments such as burning or removal of vegetation?
6. Is it necessary to remove soil? Or, can substantial differences be obtained by mixing it on site to partially bury the upper horizon soils?

7. Given the mix of soil and vegetation types within the site of a proposed reservoir, can experimental studies be used to prioritize which areas receive preflooding treatments?

5.3.2 Experimental Approaches

Most of the above questions require a characterization of the soil/vegetation "type". Since microbial activity is thought to be a function of both the organic content and degradability of the soil/vegetation, BOD was suggested as a possible integrating measure of these characteristics. While this appears to offer some advantage, differences in methylation/demethylation activity for a given level of microbial activity may limit the value of this approach. If possible, a more direct measure of the effect on fish mercury concentrations (such as actual rates of accumulation) should be sought.

Regardless of how soil/vegetation is characterized, there are several alternative experimental approaches. These include, but are not necessarily limited to: additions of various soil/vegetation types to microcosms or enclosures; treatment of soil or vegetation to simulate possible mitigative measures; and comparisons of preflood soil/vegetation BOD with concentrations of mercury in fish from different reservoirs.

5.3.3 Issues Related to Study Design

In finalizing the study design, the project team considered a number of issues. Though the following list is by no means exhaustive, it does raise important issues which may ultimately affect the utility of any proposed research. The list is therefore of use not only to this project, but also to other researchers who may undertake experimental studies of this problem in the future.

1. What technique should be used to determine the BOD of preflooded soils?

Considerable work has been done by terrestrial soil scientists with regard to BOD, but are the techniques used appropriate to the problem of methylation in flooded soils? Should the soils be simply flooded or should they be inoculated with water from reservoirs with an existing mercury "problem"? Over what time period should they be incubated?

2. Will the experiments allow us to compare results obtained from in-situ enclosures with those from microcosms? What variables should be compared?
3. How can one simulate soil stripping as a mitigative measure? Can this be done by adding lower horizon (B/C) soil to an enclosure? If so, how much must be added (e.g., sufficient of seal the existing sediment)?
4. When performing enclosure experiments, to what extent are the results influenced by working in a reservoir with an existing Hg "problem" as opposed to some other lake? Can/should this be addressed by replicating experiments in more than one reservoir?
5. In view of the variance which may be expected to be induced from other factors, e.g., temperature, oxygen, etc., to what degree are enclosure experiments between different reservoirs (or within different parts of one reservoir) actually representative of differences between soil/vegetation types? With respect to this variation, does the control of external variables offered by microcosm studies outweigh the disadvantage of an "unnatural" setting?
6. How much variance in BOD is associated with the depth at which the soil sample is taken? Can variance measures help to assess how much soil needs to be stripped?

7. At what rate do micro-organisms colonize microcosms? Over what time course should experiments be run? What merit (reduced variance, shortened time course) might be anticipated from inoculating microcosms with water (/sediment) from existing reservoirs?
8. During the workshop, it was suggested that soil type influences bioturbation rates through both physical and chemical characteristics (particle size, compaction, organic content). In view of this and the relative inability to control benthic community development other than by means which are also directly related to soil/vegetation effects (e.g., removal, capping, etc.), the merits of separate experiments to examine the details of bioturbation are doubtful. Nevertheless, consideration should be given to the variation in enclosure or microcosm experiments which may arise from differences in benthic community. Can/should this be addressed through microcosm studies? Should all such studies include benthic invertebrates to simulate a possible maximum effect? Is it easier to include or to exclude benthic invertebrates?
9. Are microcosm studies best performed in the laboratory under constant conditions of light, temperature, etc. or should some microcosm work be considered under field conditions similar to those encountered with enclosure experiments?

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